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(54) Process for the Production of High Alumina Hollow Spheres[3]

(57) The invention concerns a process for the production of high alumina hollow spheres with a diameter of up to 6 mm, for the refractory, chemical or abrasives industry. The goal of the invention is the tailored production of high alumina hollow spheres having certain properties which are in accordance with the respective application-technological values, without additional equipment expenses. Object of the invention is the development of a process which makes possible for high alumina hollow spheres to be produced from an electrofusion, through blowing[4], such that the goal of the invention is achieved. The process steps consist in the production of a melt of a high alumina material, which comprises nitride-bonded nitrogen, preferably in the form of aluminum nitride and/or oxynitrides, in a process-technologically adjustable amount and the blowing of the mentioned melt through which hollow spheres are obtained with certain physical and chemical characteristic values.

[1] *Academy of Sciences of the GDR*
[2] *Central Institute for Inorganic Chemistry*
[3] or *Hollow Spheres With High Alumina Content*
[4] in metallurgy, *verblasen* could also be translated as *converting* or *convertering*.

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Area of Application for the Invention

The invention concerns a process for the production of high alumina hollow spheres with a diameter of up to 6 mm. Such hollow spheres are needed in particular in the refractory, chemical and abrasives industry.

Characteristic of Known Technical Solution

Described in US-PS 2,136,096 is the production of hollow-sphere-like structures for the refractory industry, which are supposedly capable of being obtained through the blowing of melts of high-melting oxides like Al_2O_3 or spinels by means of air or [water] vapor. DT-PS 628,936 proposes the production of thin-walled hollow spheres by blowing a corundum melt with air or [water] vapor. According to GB-PS 248,360, GB-PS 262,405, and DT-PS 528,462 and DT-PS 537,894, respectively, small hollow spheres are produced from Al_2O_3 in conjunction with the electrofusion purification of the alumina for the extraction of aluminum.

The basic disadvantage of the processes mentioned consists in that the strength, wall thickness and particle-size distribution of the high alumina hollow spheres only accidentally agree with the required application-technical values and accordingly cannot be suitably influenced process-technologically.

In a number of further patent documents (e.g., US-PS 1,977,406; US-PS 3,104,164; US-PS 3,465,361; DT-AS 1,061,298; DT-PS 1,131,853 or DT-OS 1,660,260) and publications (e.g., Martin, R: Industr. Ceram. 1973, No. 659, p. 81 ff. or Hashimoto Kazuhiko; Ceramics Jap. 6 (1971) 11, p. 893 ff. or Gilman, W.S.: Amer. Ceram. Soc. Bull. 46 (1967) 6, p. 593 ff. or Ggaody, A.N. et al.: Ogneupory 41 (1976) 9, p. 47 ff.) it has been proposed to produce improved hollow spheres via instrumental manipulation, in particular blast[5] molding. These methods, too, have until now lead to no satisfactory process-technological influencing of the properties of the hollow spheres and moreover require a considerable additional equipment expense.

[5] or *jet molding*

Goal of the Invention

The goal of the invention is the tailored production of high alumina hollow spheres with certain properties such as, in particular, strength, wall thickness, diameter and particle-size distribution, which agree with the respective process-technological values without novel or additional equipment expenses.

The Means for Attaining the Technical Object of the Invention

It is the object of this invention to develop a process by means of which it is possible to produce high alumina hollow spheres from an electrofusion through blowing such that the goal of the invention is reached.

Characteristics of the Invention

The production of high alumina hollow spheres with a diameter of up to 6 mm and properties variable in a targeted way succeeds if nitride-bonded nitrogen, preferably in the form of aluminum nitride and/or oxynitrides, are present in process-technologically adjustable amounts within the electrofusion of the high alumina material to be blown.

It has emerged that 1 to 18 wt.% of the nitride-bonded nitrogen should advantageously be comprised in the electrofusion. The utilization of melts with higher contents of nitride-bonded nitrogen of the structure mentioned for the production of hollow spheres is in principle possible and producible according to the process, but the yield and the quality of the high alumina hollow spheres drops with increasing nitride contents. With nitride contents of above 30 wt.% in the melt, only compact porous particles form during the blowing.

The fraction in the electrofusion of the nitrides mentioned can be added to the mixture in the form of aluminum nitride, as well as adjusted in it directly through chemical conversion, which is more advantageous for the process. The latter succeeds easily under reductive conditions in the presence of gases comprising nitrogen, at normal or above normal pressure of 100 kPa to 600 kPa between 1950°K to 2500°K, more favorably between 2200°K to 2350°K.

According to the process, the reductive conditions during the melting process are created through the addition to the mixture of reduction agents, preferably of up to 20 wt.% carbon as coke. The types of coke common in technology may be used.

Higher pressures of the gas comprising nitrogen may be used, but lead to no technologically improved results.

Even though the mechanism of the nitride formation in electrofusions of high alumina materials has until now not yet completely been clarified, whereby the only concurrently certain thing is that atomic nitrogen is not notably involved in the reactions, the process conditions listed

- chemical composition of the electrofusion and its temperature,
- the presence of reducing agents,
- the presence of gases comprising nitrogen and their pressure, as well as
- the melting process

allow for a technically sufficiently accurate and targeted variable adjustment of the content of nitride-bonded nitrogen. Through that it becomes possible to produce high alumina hollow spheres with properties like strength, wall thickness and/or particle-size distribution adjustable in a targeted way by blowing the melt according to the process by means of air or water vapor. The nitride present in the melt partially or completely breaks down during the blowing process, whereby the released N_2 expands, as is well known, the melt droplets present.

The high alumina hollow spheres produced according to the process consist of

50 to 100 weight % Al_2O_3
0 to 50 weight % ZrO_2 and/or Cr_2O_3 and/or MgO
0 to 10 weight % SiO_2 as well as
0 to 3 weight % impurities, in particular TiO_2, Fe_2O_3, CaO, R_2O or nitride.

The process according to the invention for the production of high alumina hollow spheres can be performed in essentially known facilities. Novel or additional equipment expenses are thus not necessary.

Examples of Embodiment

The invention is explained more closely by means of the following examples of embodiment, whereby the invention is not restricted to these examples.

Example 1

4000 g of calcined alumina according to TGL[6] 7750 and 400 g of aluminum nitride (produced according to D. Serpek, Z. anorg. Chem. 27 (1914) 1, p. 41) are mixed intimately and then melted at 2250°K in a graphite crucible in an electric-arc furnace with immersed electrodes. The melt obtained was blown into hollow spheres by means of compressed air (300 kPa). Their properties may be gathered from the Table.

Example 2

An intimate mixture of 50 kg of calcined alumina according to TGL 7750 and 0.5 kg petroleum coke with a particle size fraction of up to 2 mm was melted within 30 min at 2250°K in a closed electric-arc furnace. 1.5 m^3 of technical grade nitrogen is additionally introduced during this time. A portion of the obtained melt was quenched and 3 wt.% of AlN were found in it through radioscopy. The greater part of the melt was blown with compressed air of 300 kPa into hollow spheres. The relevant technical characteristic values of these hollow spheres are indicated in Table 1.

Example 3

A mixture of 50 kg of calcined alumina according to TGL 7750 and 1.5 kg coke with a particle size fraction of up to 2 mm was melted and processed as in Example 2. The quenched material comprised 10 wt.% AlN; the hollow spheres had the characteristic values reported in Table 1.

[6] former GDR standard

Table 1: relevant properties of high alumina hollow spheres

Particle size in mm	Bulk Density in g/cm³				Cylinder Strength [under Compression] in kp/cm² according to ASMW[7] = B 44			
	Commercial Product X	Example 1	Example 2	Example 3	Commercial Product X	Example 1	Example 2	Example 3
0.5 to 1.0	0.85	0.98	0.80	1.00	16.5	68.0	25.2	68.2
1.0 to 2.0	0.65	0.96	0.66	0.98	13.0	46.0	16.2	46.8
2.0 to 3.0	0.64	0.82	0.62	0.83	6.0	22.0	8.4	21.8
3.0 to 4.0	0.54	0.70	0.50	0.68	4.5	10.0	5.1	11.0
4.0 to 5.0	--	0.40	0.38	0.42	--	6.0	3.2	6.4

Chemical composition in wt.%		
Al_2O_3	99.6	98.9
SiO_2	0.01	0.5
Fe_2O_3	0.03	0.1
CaO	0.01	0.25
R_2O	0.3	0.10
N as nitride	--	0.20

[7] Amt für Standardisierung, Messwesen und Warenprüfung = Agency for Standardization, Metrology and Commodities Testing of the former German Democratic Republic

Claim of the Invention

Process for the production of high alumina hollow spheres with a diameter of up to 6 mm from an electrofusion through blowing, characterized in that hollow spheres with a chemical composition of

50 to 100 weight % Al_2O_3

0 to 50 weight % ZrO_2 and/or Cr_2O_3 and/or MgO

0 to 10 weight % SiO_2 as well as

0 to 3 weight % impurities, in particular TiO_2, Fe_2O_3, CaO, R_2O or nitride.

are produced through blowing by means of air or water vapor from a melt opened-up in the electric-arc furnace from a high alumina material which comprises 1 to 20 wt.% nitride-bonded nitrogen, preferably in the form of aluminum nitride and/or oxynitrides, which is either added to the mixture of the high alumina material in the form of technical grade aluminum nitride or in particular produced between 1950°K to 2500°K, preferably between 2200°K to 2350°, in the electrofusion in the presence of 1 to 20 wt.% carbon, silicon, silicon carbide, aluminum or aluminum carbide as reduction agents, preferably carbon which is advantageously mixed in as coke into the high alumina material, and [the presence] of gases comprising nitrogen at normal or above normal pressure of 100 kPa to 600 kPa.